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APPLICATION NUMBER: 60/565,053

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Preliminary Classification  
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17858 U.S. PTO  
60/1565053

## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of: John Mak, Richard B. Nielsen, Thomas King Chow, Morgan Oliver, and Vincent Wai Wong

For: Additional Methods and Configurations for Acid Gas Enrichment and Sulfur Recovery

Mail Stop Provisional Patent Application  
Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

**COVER SHEET FOR FILING PROVISIONAL APPLICATION**  
(37 C.F.R. § 1.51(c)(1))

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 C.F.R. § 1.51(c)(1)(i). The following comprises the information required by 37 C.F.R. § 1.51(c)(1):

1. The following comprises the information required by 37 C.F.R. § 1.51(c)(1):

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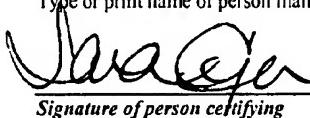
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2. The names of the inventors are (37 C.F.R. § 1.51(c)(1)(ii)):

1. John Mak
2. Richard B. Nielsen
3. Thomas King Chow
4. Morgan Oliver
5. Vincent Wai Wong

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4. The title of the invention is (37 C.F.R. § 1.51(c)(1)(iv)):

Additional Methods and Configurations for Acid Gas Enrichment and Sulfur Recovery

5. The name, registration, customer and telephone numbers of the practitioner are (37 C.F.R. § 1.51(c)(1)(v)):

Name of practitioner: Martin Fessenmaier  
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6. The docket number used to identify this application is (37 C.F.R. § 1.51(c)(1)(vi)):

Docket No. 100325.0253PRO

7. The correspondence address for this application is (37 C.F.R. § 1.51(c)(1)(vii)):

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8. Statement as to whether invention was made by an agency of the U.S. Government or under contract with an agency of the U.S. Government. (37 C.F.R. § 1.51(c)(1)(viii)).

This invention was NOT made by an agency of the United States Government, or under contract with an agency of the United States Government.

9. Identification of documents accompanying this cover sheet:

A. Documents required by 37 C.F.R. § 1.51(c)(2)-(3):

Specification:	No. of pages	8
Drawings:	No. of sheets	6

10. Fee

The filing fee for this provisional application, as set in 37 C.F.R. § 1.16(k), is \$160.00 for other than a small entity.

11. Fee payment

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## **ADDITIONAL METHODS AND CONFIGURATIONS FOR ACID GAS ENRICHMENT AND SULFUR RECOVERY**

### **Field of The Invention**

5        The field of the invention is gas processing and sulfur removal, especially as it relates to enrichment of an acid gas stream with high CO<sub>2</sub> content and a tail gas from Claus plant.

### **Background of The Invention**

10      There are numerous sources of natural or synthesis gas known in the art, and almost all of them contain H<sub>2</sub>S in various quantities that require at least partial desulfurization prior to further processing or release into the atmosphere. For example, natural gas, refinery gas, synthesis gas (*e.g.*, from gasification of residual oil or coke), or Fischer-Tropsch gas-to-liquids process (GTL) gases often contain H<sub>2</sub>S in significant amounts that would interfere with downstream processes. Furthermore, the sulfur content in the tail gas from the Claus reactors typically requires treatment before releasing the tail gas to the environment.

15      If H<sub>2</sub>S is present in large quantities, removal is commonly accomplished by absorption in an alkaline solvent, usually with an amine solvent. H<sub>2</sub>S is later regenerated or desorbed in a regenerator in a stripper operating at a lower pressure and elevated temperature. The acid gas from the regenerator is then typically processed in a Claus plant where the H<sub>2</sub>S is converted to elemental sulfur by sub-stoichiometric reaction with air or oxygen.

20      However, nearly all gas streams which contain H<sub>2</sub>S also contain a significant quantity of CO<sub>2</sub> and when such gases are simply scrubbed with an alkaline solution, CO<sub>2</sub> is co-absorbed with the H<sub>2</sub>S. This is particularly problematic where the ratio of CO<sub>2</sub> to H<sub>2</sub>S in the gas stream is relatively high, as complete removal of both gases will often produce an acid gas weak in H<sub>2</sub>S, which tends to cause various problems in the Claus plant. Among other things, the dilution effect of CO<sub>2</sub> in such acid gases lowers the net heating value in the acid gas and reduces the residence time in the Claus furnace, rendering sulfur conversion difficult. Moreover, such acid gases typically contain significant quantities of contaminants (*e.g.*, benzene, toluene, xylene and heavy hydrocarbons) that generally must be destroyed in the Claus furnace, which is necessary for protection of the downstream Claus reactor catalysts. Unfortunately, the CO<sub>2</sub> dilution effect in

such acid gases tends to lower the furnace flame temperature, thereby making destruction of these contaminants difficult.

In extreme cases, where the H<sub>2</sub>S content in the acid gas falls below 10%, a normal Claus reaction becomes impossible and additional costly processing steps must be employed to enhance 5 the conversion process, such as with oxygen or oxygen enriched process. Additionally, the dilution effect of CO<sub>2</sub> will increase the size of the Claus plant as the plant size is predominantly controlled by the total volumetric flow of acid gas.

Where the acid gas is unsuitable as feed to a Claus plant, preprocessing using a selective acid gas removal process is frequently necessary. In a typical preprocessing operation, two gas 10 streams are produced via selective absorption of H<sub>2</sub>S from the acid gas and subsequent stripping of the rich solvent. Thus, one gas stream predominantly comprises CO<sub>2</sub> and ppmv levels of H<sub>2</sub>S, that can be sent to a thermal oxidizer or incinerator, prior to being discharged to the atmosphere. The other gas stream is enriched in H<sub>2</sub>S and is then processed in a Claus plant, which typically 15 must use highly reactive catalysts or followed by a tail gas treatment unit to meet the high sulfur conversion requirement in compliance with today's environmental regulations.

Known processes for selective H<sub>2</sub>S removal from high CO<sub>2</sub> gases include the Stretford, LOCAT, and/or Sulferox process. These processes employ complex catalyst-based chemistry to oxidize H<sub>2</sub>S directly to sulfur. However, these units are often complex, difficult to operate, and are limited to relatively small capacity. Alternatively, various known amine based solvents 20 capable of selectively removing H<sub>2</sub>S can be used. For example, selective absorption processes can be based on variations of tertiary amines (e.g., those comprising formulated methyldiethanol-amine (MDEA), sterically hindered tertiary amines, and other amine-organic solvent blends). Such solvents, particularly when combined with special absorber internal designs will minimize 25 co-absorption of CO<sub>2</sub> (typically, such processes can concentrate the H<sub>2</sub>S content by a factor of three to five fold). Other processes for selective H<sub>2</sub>S removal include the use of a variety of sterically hindered tertiary amino compounds described in U.S. Pat. Nos. 4,405,580.

In still further attempts to increase selectivity of absorption, special tray configurations can be employed to reduce the contact time with CO<sub>2</sub> to achieve the required selectivity. These

special equipments are designed to slow down the mass transfer between amine with CO<sub>2</sub> relative to that with H<sub>2</sub>S, thereby improving the selectivity process. For example, U.S. Pat. Nos. 4,278,621 and 4,297,329 and 4,678,648 describe special tray and packing designs in minimizing CO<sub>2</sub> contact time. Unfortunately, the use of such processes and/or devices in most cases results  
5 in only marginal benefit for treating a diluted acid gas stream.

Alternatively, as described in U.S. Pat. Nos. 4,198,386 and 4,093,701, selectivity is achieved by varying gas flow-rates using a plurality of absorption columns, and splitting the absorber column into a number of absorption zones with controlled flow-rates of lean amine solvent. However, such systems are generally not effective to treat a very diluted acid gas at low  
10 pressures. They are also often costly and complicated to operate. In yet further attempts to increase selectivity, H<sub>2</sub>S absorption may be enhanced via temperature control. Generally, a reduction in absorption temperature slows the CO<sub>2</sub> absorption rate. However, the cost and complexity of operating a refrigeration unit renders such an option often uneconomical.

Even where selective acid gas absorption is practiced with concurrent conversion of H<sub>2</sub>S to elemental sulfur in Claus plant, the residual sulfur content in Claus plant tail gases frequently poses additional problems. Among other things, the Claus plant tail gas often contains substantial quantities of H<sub>2</sub>S and fails to meet the overall sulfur recovery requirement and comply with emission standards. Numerous configurations are known in the art to reduce the sulfur content of such tail gas. However, most of such configurations are relatively complex and costly.  
15

20 Therefore, and especially where a diluted acid gas feed is encountered, currently known methods and configurations are often neither suitable nor economical. Thus, there is still a need to provide improved configurations and methods for selective acid gas enrichment.

#### Detailed Description

The inventors generally contemplate integrated configurations and methods of selective  
25 H<sub>2</sub>S absorption and sulfur recovery from various gases comprising H<sub>2</sub>S and CO<sub>2</sub>, and especially from gases in which H<sub>2</sub>S is diluted.

In one aspect, and with respect to selective H<sub>2</sub>S absorption, contemplated configurations employ an amine solvent (*e.g.*, methyldiethanolamine based solvent or sterically hindered tertiary amines for preferential H<sub>2</sub>S absorption), and a dilute acid gas is first contacted with the lean solvent for selective removal of H<sub>2</sub>S, thereby producing (1) an overhead CO<sub>2</sub> vapor with ppm level of H<sub>2</sub>S suitable for disposal in an incinerator, and (2) a H<sub>2</sub>S rich solvent that is processed in a regenerator. The regenerator produces a H<sub>2</sub>S enriched acid gas, a portion of which is contacted by a second amine contactor, preferably using lean amine from the regenerator and semi-lean amine from the third absorber, producing an overhead CO<sub>2</sub> vapor with ppm level of H<sub>2</sub>S suitable for disposal in an incinerator, and a H<sub>2</sub>S rich solvent that is recycled to the regenerator.

In an especially preferred aspect, the acid gas enrichment process is integrated with a Claus plant and a catalytic hydrogenation and quench unit, wherein the H<sub>2</sub>S enriched acid gas from the selective absorption process is sent to the integrated Claus unit. With respect to configurations and methods for selective H<sub>2</sub>S absorption from an acid gas comprising CO<sub>2</sub>, the same considerations as described in our copending U.S. provisional patent application with the title "Methods and Configurations for Acid Gas Enrichment" (filed on or about 01/20/2004 (John Mak et al.), and incorporated by reference herein) apply.

In particularly contemplated integrated configurations, the tail gas from the Claus plant is passed through a catalytic hydrogenation reactor and a quench column forming a tail gas containing a dilute concentration of H<sub>2</sub>S. The tail gas is treated in a third absorber, using lean solvent produced from the regenerator, producing an overhead CO<sub>2</sub> vapor with ppm level H<sub>2</sub>S suitable for incinerator, and a H<sub>2</sub>S rich solvent that is either used as a semi-lean solvent to the first and second amine absorber or recycled to the regenerator. Thus, it should be recognized that contemplated configurations lower the overall treating and sulfur recovery costs while minimizing emission problems. Based on various calculations, the inventors discovered that sulfur can be recovered up to 99.7% (and even higher) with significantly reduced capital and operating costs as compared to heretofore known configurations. Therefore, viewed from another perspective, the inventors contemplate an integrated three amine absorption stage enrichment

process that enriches H<sub>2</sub>S in diluted acid gas to about 75% while achieving a high sulfur recovery.

The contemplated configurations can also be applied to the case without integration of the tail gas from the Claus unit. In this case, the same configuration of the first two absorbers applies  
5 and the diluted acid gas can be concentrated to about 75% H<sub>2</sub>S, with the Claus unit independently located downstream of the amine units.

Figure 1 shows an exemplary integrated configuration according to the inventive subject matter. The inventors discovered that combinations of an enrichment unit and a third absorber processing the tail gas from the Claus unit can effectively achieve a 99.7% or higher sulfur  
10 recovery with significantly reduced equipment.

Here, a two-stage Claus reactor system is used to process the enriched acid gas stream 18. It should be appreciated that a conventional sulfur plant without a tail gas treatment option would typically require four-stage Claus reactors equipped with special burner design, highly reactive catalysts, and additional processing steps in order to achieve desirable BTX (benzene, toluene  
15 and xylenes) destruction and 99% sulfur recovery. In contrast, contemplated integrated tail gas absorption configurations significantly reduce overall cost when compared to conventional plants. The effluent gas from the Claus unit (stream 30), typically comprising trace quantities of sulfur oxides and unconverted H<sub>2</sub>S, is processed in a hydrogenation and quench unit 71. The quenched hydrogenated gas is scrubbed in the third scrubber 72 using lean amine stream 32 that  
20 is supplied from the lean amine header. The tail gas absorber overhead vapor stream 33 comprising trace levels of H<sub>2</sub>S can be routed to incinerator for disposal.

The rich amine stream 34 from the third absorber is pumped by amine pump 73 forming stream 35 which is then combined with the rich amine stream 7 from the first absorber 51, forming stream 36. The combined stream is heated in the lean/rich exchanger 55 and fed to the  
25 common regenerator as stream 8.

Alternatively, Figure 2 shows another exemplary integrated configuration with a Claus unit. In this configuration, the semi-lean solvent 35 from the tail gas absorber 72 is re-used in the

second absorber 52 and fed to the mid section of the second absorber. With this arrangement, the total solvent circulation and regeneration duty are significantly reduced, resulting in lower capital and operating costs of the system.

Figure 3 shows yet another exemplary integrated configuration with a Claus unit. This configuration is similar to Figure 2 with the exception that a portion of the semi-lean solvent stream 7 from the first absorber 51 is re-used as stream 74. This semi-lean solvent is cooled in a cooler 73 to about 100°F forming stream 75. This cold semi-lean solvent is routed to the lower section of the second absorber 52. This configuration further reduces the solvent circulation and regeneration duties.

In still further preferred aspects of the inventive subject matter, it should be recognized that the acid gas stream from the regenerator can be split into a first and second stream to achieve even better H<sub>2</sub>S removal and/or improve cost effectiveness. Such configurations may include an integrated Claus plant as depicted in the exemplary configuration of Figure 4, or operate as acid gas removal plant without integrated Claus plant as depicted in the exemplary configuration of Figure 5.

With reference to Figure 4 where the Claus plant is integrated into the acid gas removal plant, the acid gas stream 14 from the regenerator is split into two portions: Stream 14 and stream 17. Stream 14 is fed to the bottom of absorber 72 (tail gas absorber). The hydrogenated tail gas stream 31 is fed from the Claus plant hydrogenation and quench unit to the mid section of the absorber 72. It should be recognized that such split flow configuration takes advantage of the semi-lean amine stream 200 from the top section for further absorption in the lower section of the absorber 72. Alternatively, stream 31 and stream 17 can be combined and fed to the bottom of the absorber 72. Consequently, it should be appreciated that such configurations have eliminated the requirement of previously required absorber 52, resulting in significant cost savings.

Similarly, without integrated Claus plant as shown in Figure 5, the acid gas stream 17 in the split-flow configuration is divided into two streams, stream 90 and 91. Stream 91 can be optionally split to stream 94 and stream 93. Stream 94 can be combined with feed gas stream 1 forming stream 92 and fed to the absorber 51 while stream 93 can be optionally fed

independently to the bottom of the absorber. Recycling at least a portion of the acid gas stream to the feed gas is particularly advantageous to further enhance the H<sub>2</sub>S content in the enriched gas stream. Moreover, it should be recognized that such configurations may be especially useful where the flow of feed gas is variable with varying H<sub>2</sub>S content.

5        Where reduction of solvent circulation is particularly desired, configurations according to Figure 6 may be implemented. Here, the stream 35 from the tail gas absorber bottoms pump 73 is split into two portions: Stream 101 and stream 102. The split ratio of streams 101 to 35 varies from 0.2 to 1, and it should be recognized that the exact set point depends on the circulation rate of stream 35, and the acid gas content of the feed streams to absorber 51. Such a configuration is  
10 particularly effective in reducing the overall solvent circulation and hence the energy requirement by using the semi-lean solvent from the third absorber to further absorb the acid gas in the feed systems operating at a higher pressure.

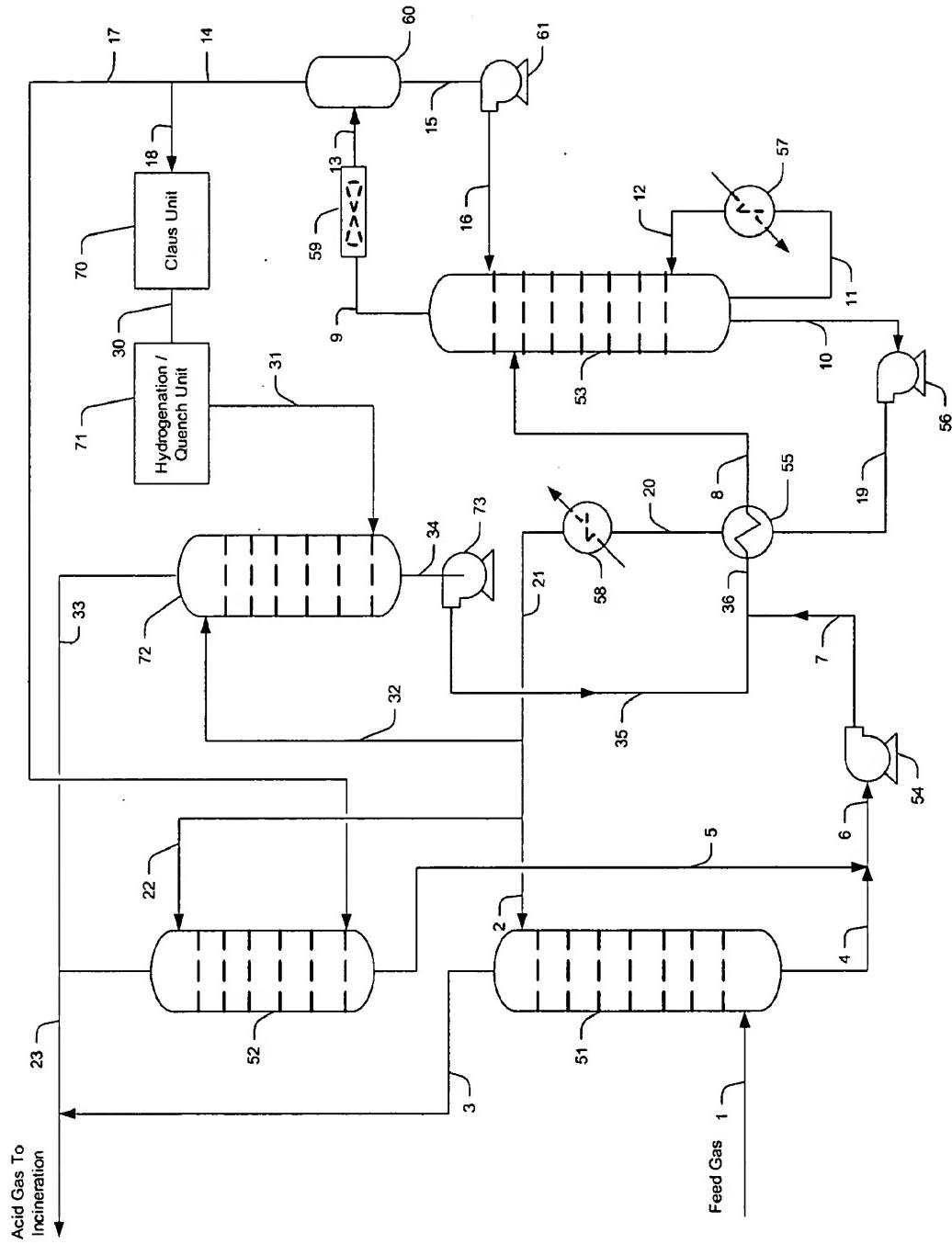
In a further modification over the configurations depicted in Figures 1-5, the enriched acid gas stream 14 from reflux drum 60 is split into two portions: Stream 17 and 18. The split 15 ratio of stream 17 to 14 varies from 0.2 to 0.8 depending on the level of enrichment required. The higher the split ratio (*i.e.*, the higher the relative flow of stream 17), more CO<sub>2</sub> will be rejected in absorber 51, which will further increase the degree of H<sub>2</sub>S enrichment from reflux drum 60. Stream 17, which has the highest concentration of H<sub>2</sub>S, is fed to the bottom of absorber 51. The higher concentration increases the acid gas loading of the solvent, thus further reducing the  
20 overall circulation requirement.

Thus, it should be particularly appreciated that configurations according to the inventive subject matter will produce an acid gas enriched in H<sub>2</sub>S from a lean H<sub>2</sub>S stream, wherein the acid gas can be enriched from about 7% to about 75% H<sub>2</sub>S. Moreover, preferred configurations allow removal of heavy hydrocarbons and BTEX components that is problematic with sulfur  
25 plant operation. Still further, it should be recognized that contemplated configurations will produce a CO<sub>2</sub> stream with low H<sub>2</sub>S content suitable for disposal in incinerators.

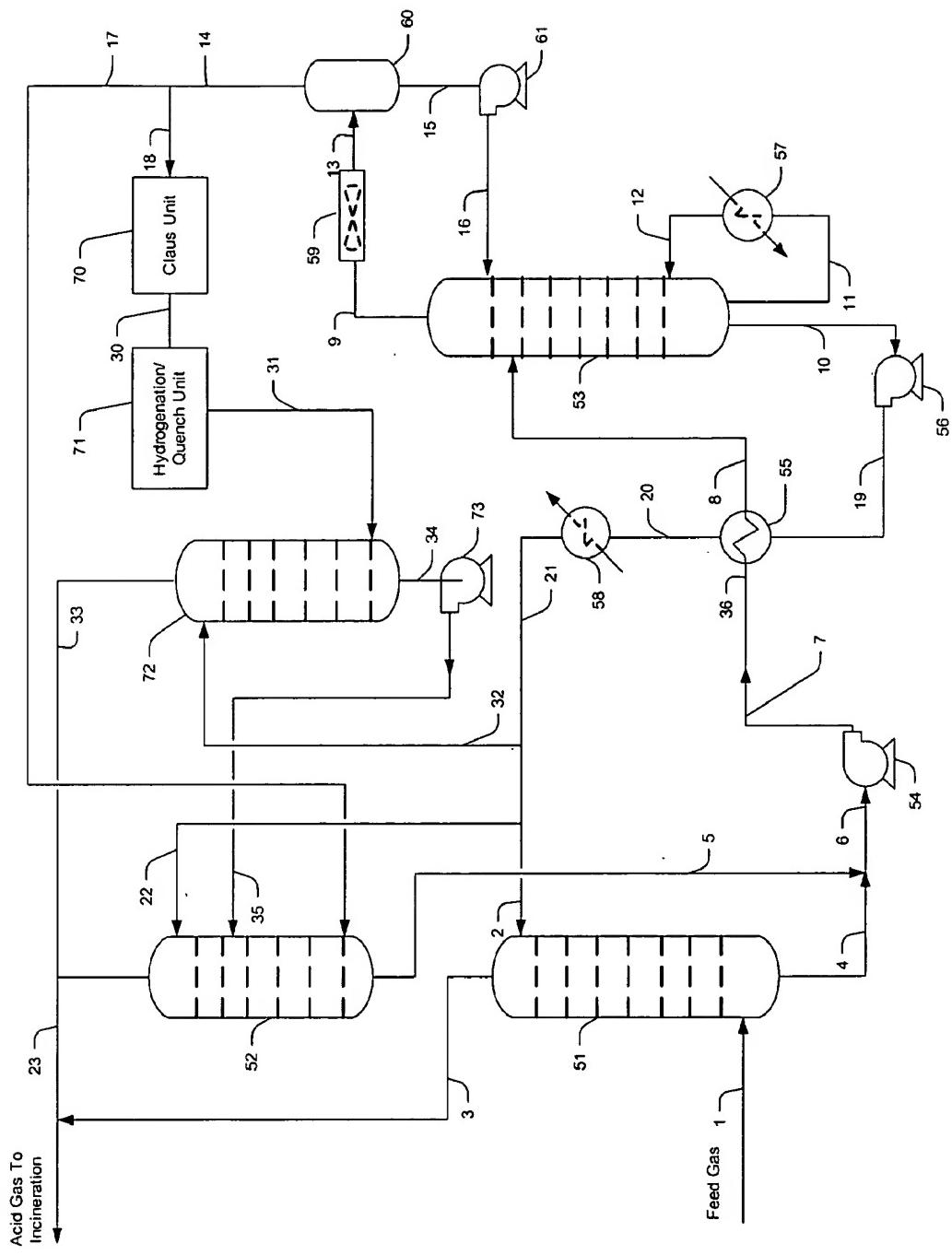
In present integrated Claus plant configurations, two otherwise necessary stages of Claus reactors can be eliminated, which substantially reduces overall plant cost. Still further,

contemplated configurations solve the problems of low H<sub>2</sub>S content and lower heating content in the acid gas where the acid gas is diluted. Therefore, difficulties associated with fuel gas firing for the Claus reaction and BTEX destruction are eliminated. It should be further recognized that contemplated configurations and processes may advantageously be employed with various gas 5 plants, sulfur plants, Gas-to-Liquid conversion plants, gasification plant, enhanced oil recovery plants, and various existing facilities that are retrofitted to meet more stringent emission requirements.

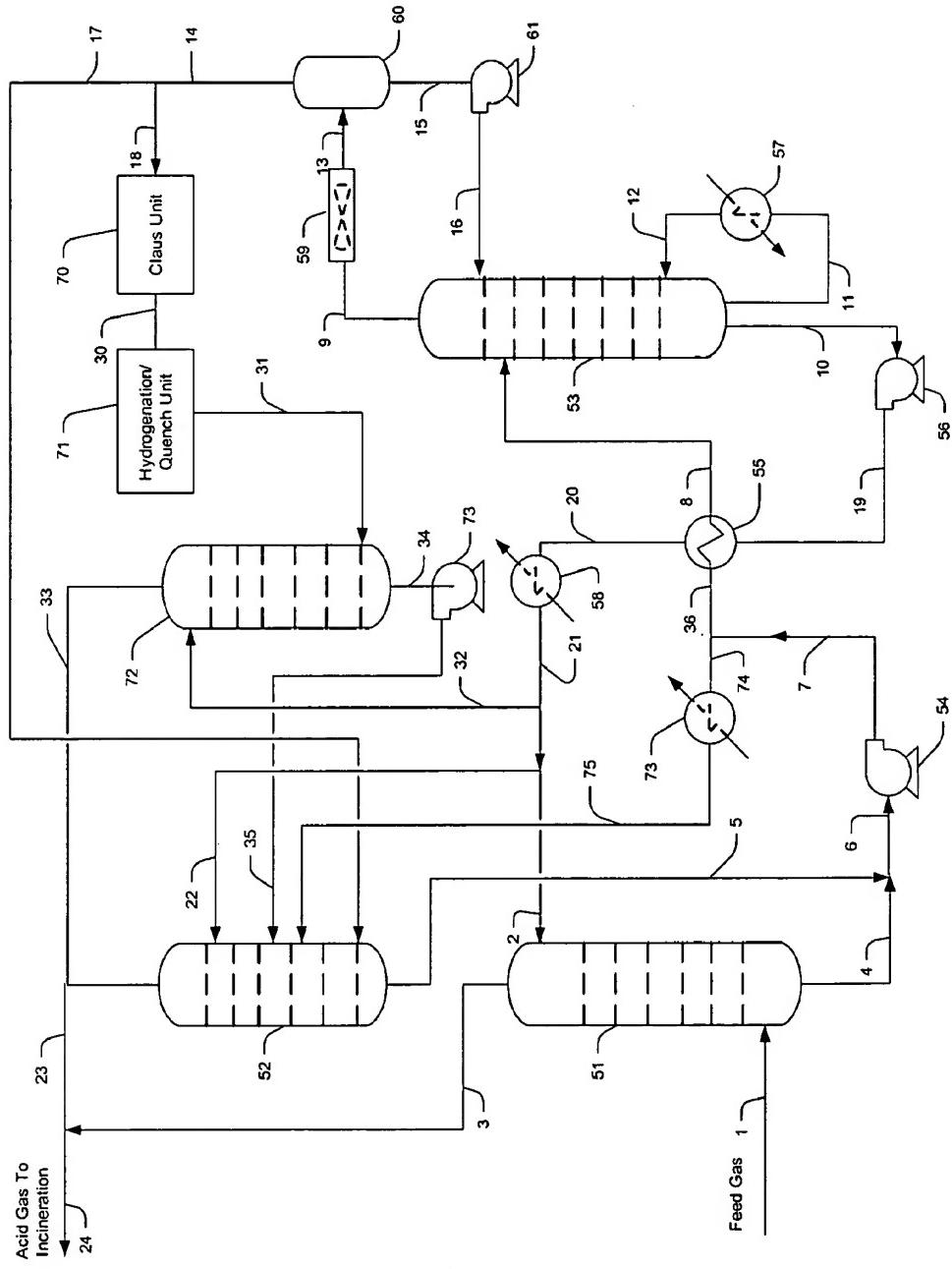
Thus, specific embodiments and applications of acid gas enrichment and sulfur recovery have been disclosed. It should be apparent, however, to those skilled in the art that many more 10 modifications besides those already described are possible without departing from the inventive concepts herein. The inventive subject matter, therefore, is not to be restricted except in the spirit of the present disclosure. Moreover, in interpreting the specification, all terms should be interpreted in the broadest possible manner consistent with the context. In particular, the terms "comprises" and "comprising" should be interpreted as referring to elements, components, or steps in a 15 non-exclusive manner, indicating that the referenced elements, components, or steps may be present, or utilized, or combined with other elements, components, or steps that are not expressly referenced.



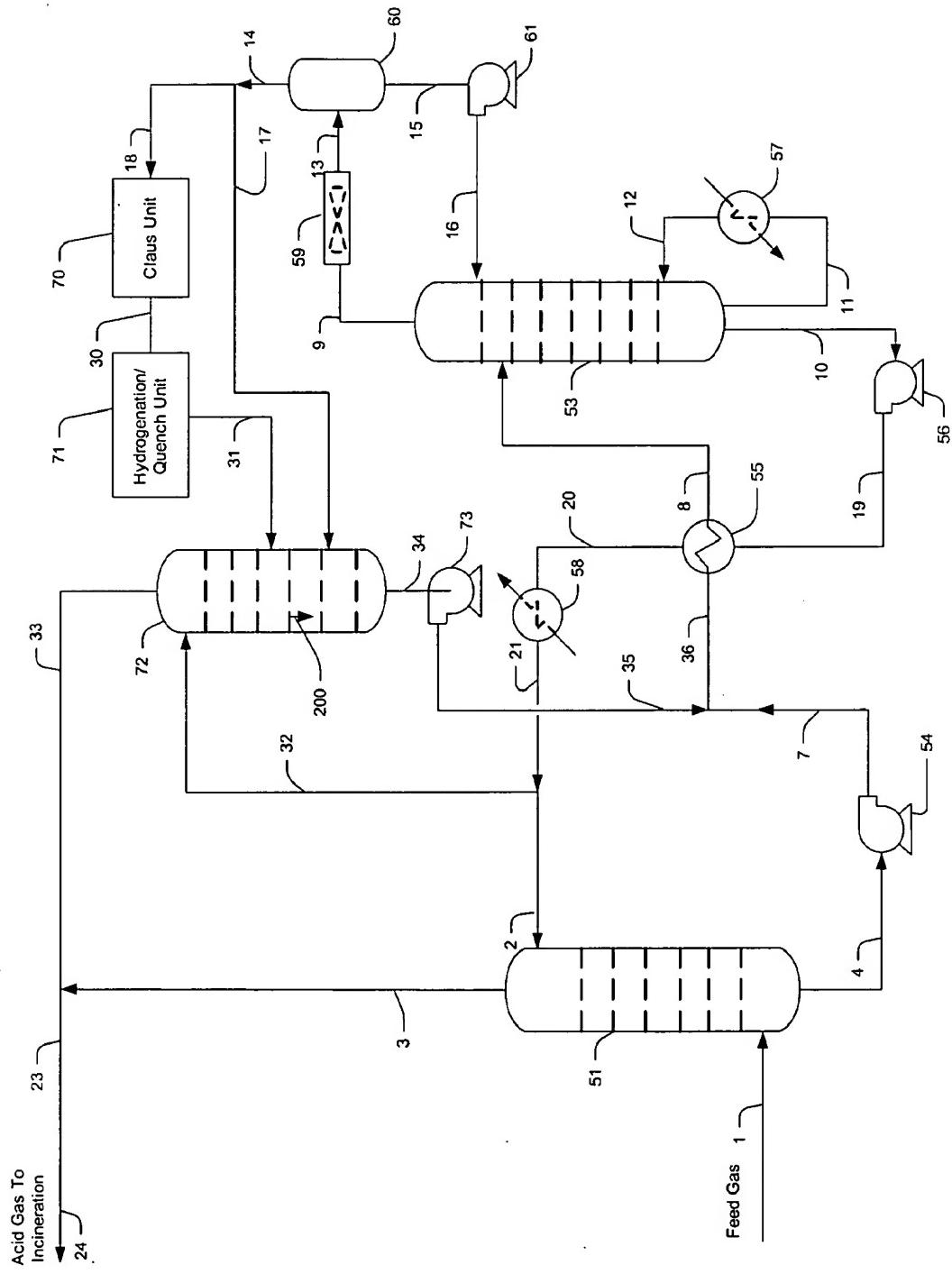
**Figure 1**



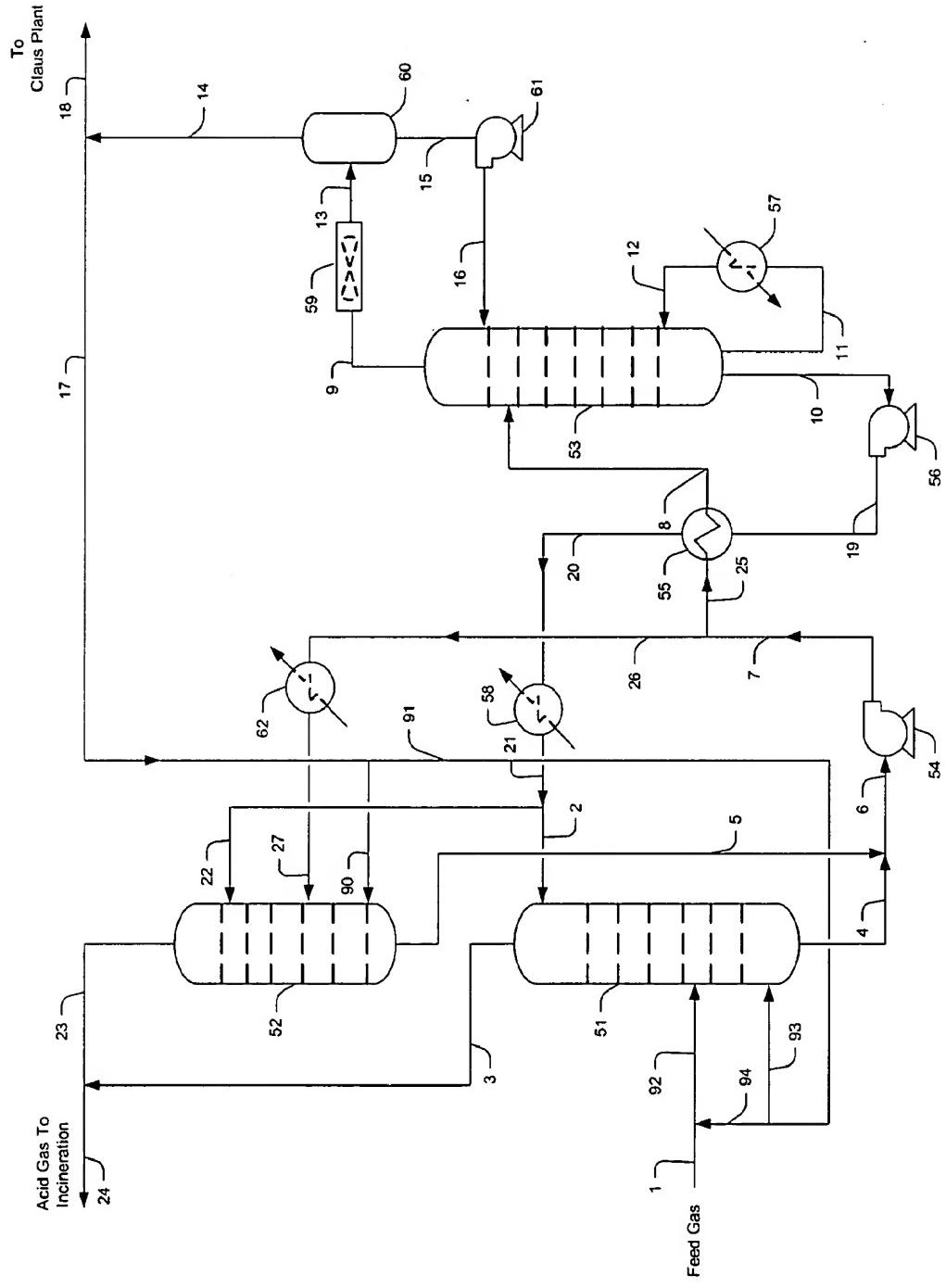
**Figure 2**



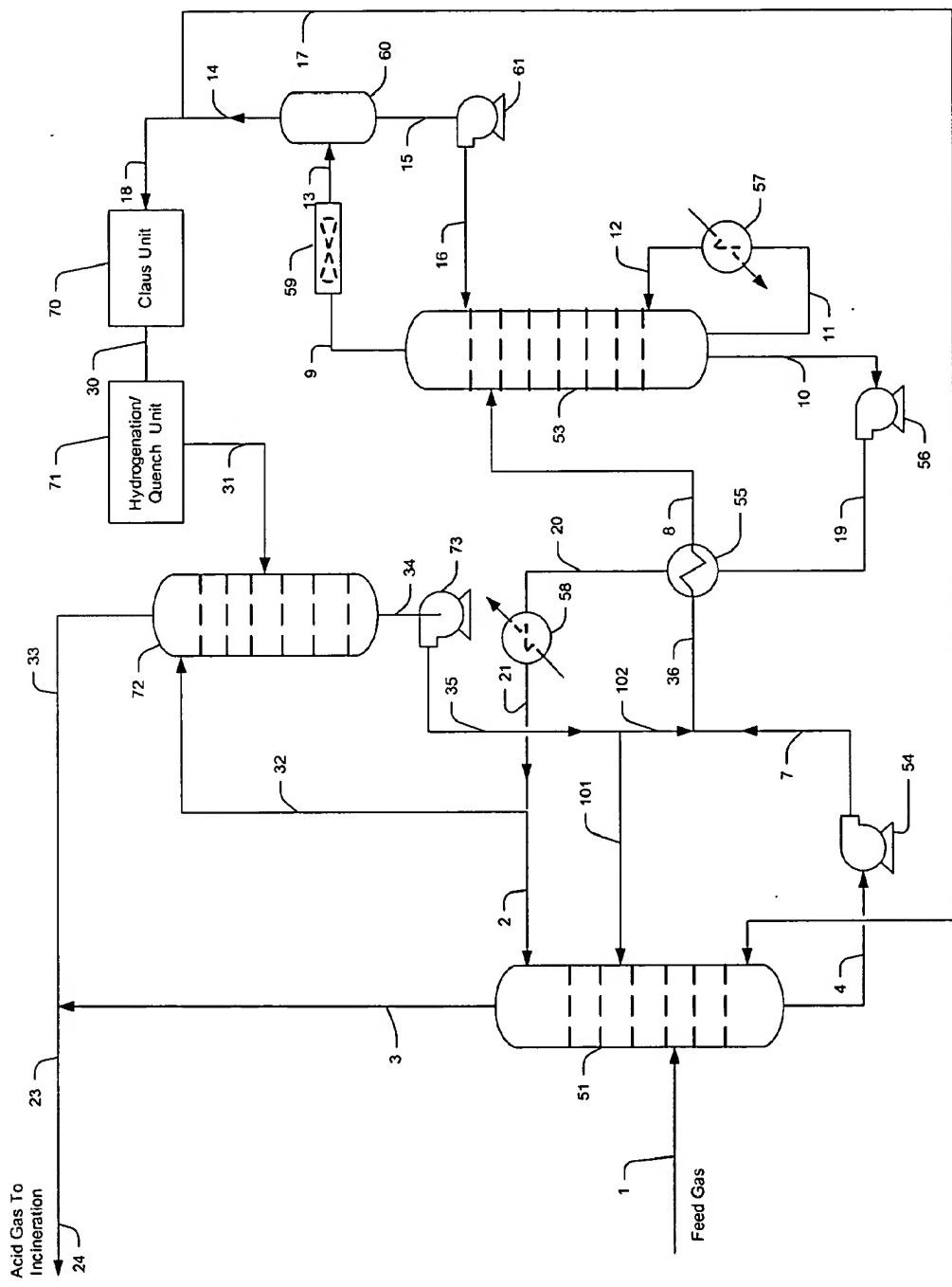
**Figure 3**



**Figure 4**



**Figure 5**



**Figure 6**